

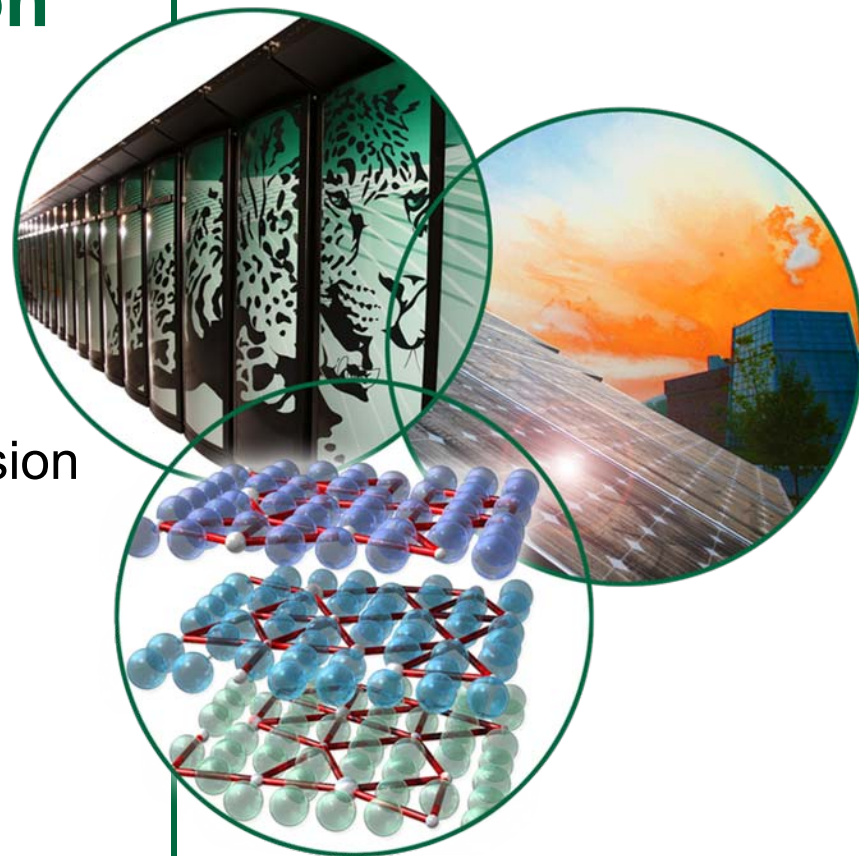
# Ultra-high Resolution Electron Microscopy for Catalyst Characterization

Project ID: pmp\_24\_allard

L. F. Allard

Materials Science & Technology Division  
Oak Ridge National Laboratory  
Oak Ridge, TN

2009 DOE Merit Review  
Crystal City, MD  
May 22, 2009



Agreement PM-9105



This presentation does not contain any  
proprietary, confidential, or otherwise  
restricted information.



## Timeline

- Project start date: 10/01/2004
- Project end date: 09/30/2010
- Percent complete: 75%

## Budget

- Total project funding
  - DOE share: \$780,000
  - Contractor share: \$80,000
- FY08 funding: \$220,000
- FY09 funding: \$99,850 (thru March 9, 2009)

## Barriers

- Development and optimization of catalyst-based aftertreatment systems are inhibited by the lack of understanding of catalyst fundamentals (*e.g., surface chemistry, deactivation mechanisms, particulate capture and oxidation*) and catalysts modeling capabilities.
- Reduce aftertreatment system costs and develop new catalyst materials for NOx and PM reduction that improve the cost effectiveness of aftertreatment systems (*e.g., eliminate the use of precious metals*).

## Partners

- Eastman Chemicals, UOP, PNNL, UT-Austin, UT-San Antonio, UNewMexico, MIT, Protochips Co., UM-St. Louis
- Proj. Lead: L. F. Allard

# Purpose of Work

- **Advance frontiers** of atomic and molecular characterizations of energy-related catalysts using world-class sub-Ångström imaging capability with EERE-funded aberration-corrected electron microscope, ultimately leading to a better understanding of factors influencing the behavior of catalytic species under use conditions, and thereby to better catalytic materials for exhaust after-treatment.
- **Develop novel** new capability for in-situ studies. Extend demonstrated unique capability for in-situ heating to development of an environmental cell capability for gas reaction studies.

# Barriers

- Catalytic process occur at the atomic level, with interactions between individual atoms, small clusters etc. We have a limited understanding of these processes. Sub-Ångström imaging in the electron microscope is the only way to obtain direct evidence of what is occurring.
- New capability for in-situ reaction studies via novel environmental cell will depend on as-yet unproven technology being developed in collaboration with Protochips Co. Success with Protochips heaters offers much promise for similar success with reaction cell fabrication.
- The quality of imaging using the E-cell concept will depend on development of ultra-thin amorphous window material (~20nm thick or less) that will maintain their integrity inside the microscope, and will not significantly degrade the imaging process.

# Approach

- Acquire and maintain the very best microscopy instrumentation for EERE catalyst/energy materials research. **Example: ACEM.**
- Develop and utilize the techniques necessary for advanced catalyst characterization. **Example: in-situ heating technology.**
- Through professional contacts, information sources such as literature and meetings, communication with UT-B and DOE program managers, determine those research areas where the microscopy program can make significant and important contributions. **Example: Support a variety of EERE programs.**
- Use the above to set immediate and long-term microscopy program goals. **Example: in-situ microscopy with environmental cell capability for reaction studies.**
- Partner with industrial and university research teams when such partnerships will benefit both parties. **Example: PNNL, UOP, UM-St. Louis, Eastman Chemicals**
- Perform research, analyze data, and promulgate results to appropriate parties.

# Performance measures and accomplishments

- Demonstrate sub-Ångström imaging capability of ACEM
- Demonstrate and utilize atomic-level imaging for studies at elevated temperatures (in-situ reactor)
- Develop new protocols for reaction studies via pseudo-*ex-situ* techniques (e.g. airlock reaction system)
- Industrial and university partnerships formed
- Publications
- Invited presentations

# Collaborators in *in-situ* microscopy of catalytic materials

- Steven Bradley, UOP Co.  
Pt/Al-Si-Ti oxides, Pt-Sn bimetallics, correlate EM and EXAFS results
- Miguel Jose-Yacamán, UTexas-San Antonio  
Au-Pd nanoparticles, Pt/carbon, fundamental studies
- Abhaya Datye, Univ. of New Mexico  
Pt-Zn/alumina methanol reforming for hydrogen production
- Charles Peden, PNNL  
Ba/alumina, Pt/alumina, NO<sub>x</sub> traps
- David Nackashi, Protochips Co.  
WFO project: *in-situ* heater and environmental cell development
- Paulo Ferreira, UTexas-Austin  
Pt-Co/carbon fuel cell catalysts, new Li-ion battery materials
- Yang Shao-Horn, MIT  
Pt surface segregation in leached Pt-Co fuel cell catalysts
- Jimmy Liu, Univ. of Missouri-St. Louis  
Pd/ZnO, PtSn/C on-board methanol reforming, direct ethanol FC
- Lou Germinario, Eastman Chemicals  
WFO project: “Atomic Scale Imaging of Gas-Metal Cluster Interactions.”
- Yong Wang, Liang Zhang, PNNL  
Pt-Re bimetallics on multiwalled CNTs for aqueous phase reforming

# Our work also supports ORNL EERE programmatic research:

- Cummins catalyst characterization CRADA (Watkins)  
(zeolites, ammonia oxidation (new 2009))
- Catalysis by First Principles (Narula et al.)  
(Pt/alumina, CO and NO oxidation)
- HTML User Program projects (Lara-Curzio)  
(bimetallic catalysts for DEFCs, methanol reforming)

## Other ORNL program collaborations:

- BES Nanocatalyst Characterization (Overbury)  
(Au/FeOx catalysts for H<sub>2</sub> purification and CO oxidation)



# JEOL 2200FS-AC

## Aberration-Corrected Electron Microscope

- Sub-Ångström resolution (0.7Å)
- Housed in Advanced Microscopy Laboratory
- Remotely operated (e.g. adjacent control room, London, Austin...)
- New thrust: in-situ studies with novel heating capabilities and developing “environmental cell” capability



# ORNL-Protochips Co. collaboration has resulted in significant advances in heater holder development

## Examples

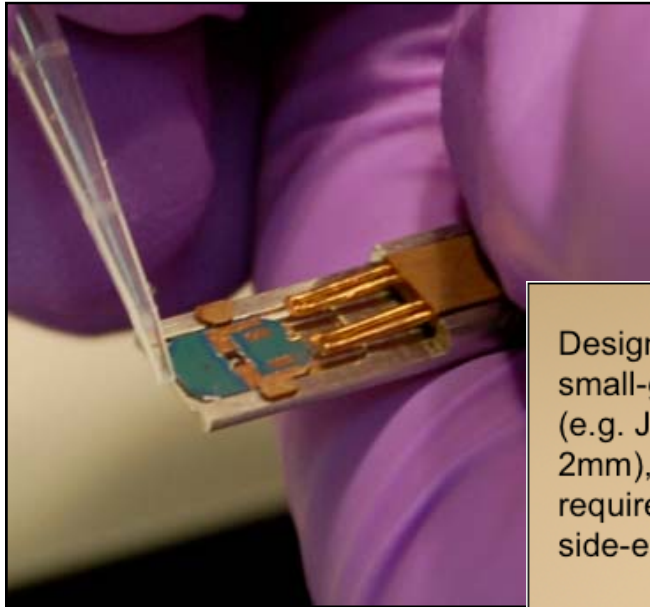
- We have built a heater holder for the new Hitachi HF-3300 field emission TEM. This holder will allow us to conduct experiments requiring energy-dispersive x-ray results, and ultimately electron holography results, only available on the Hitachi instrument.



Slot to provide x-ray path  
to detector

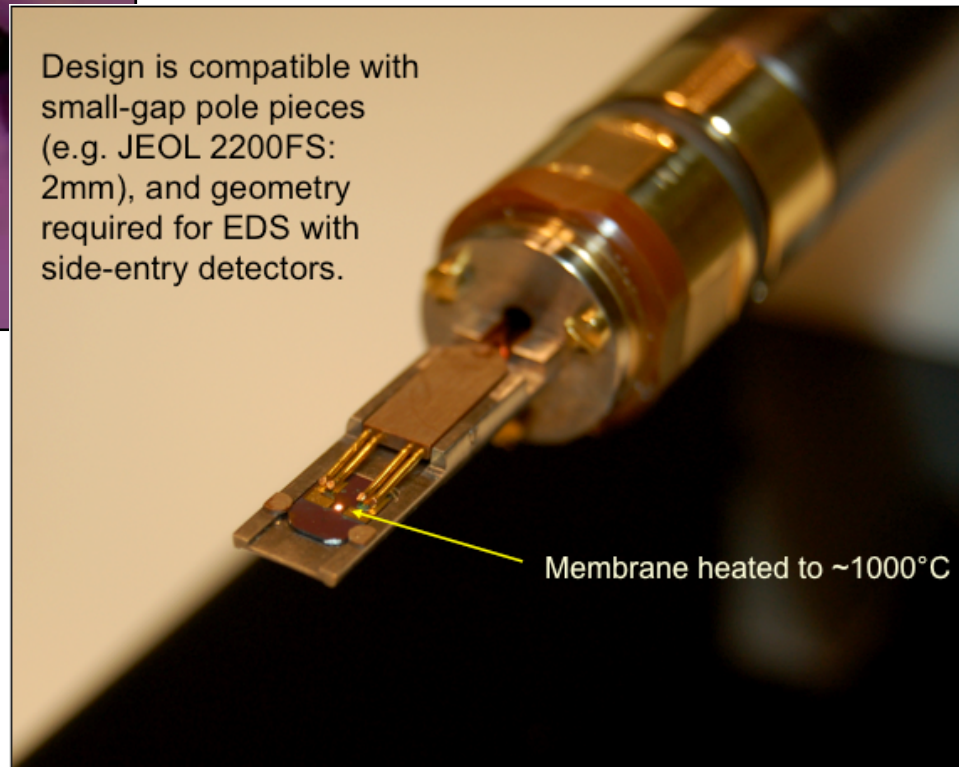
Aduro™ chip heated to  
~1000°C (glowing  
membrane)

# Commercial version of Protochips heater holder has been developed



A new Aduro™ chip design has leads on the end, and a new clamp mechanism for easy chip loading

Design is compatible with small-gap pole pieces (e.g. JEOL 2200FS: 2mm), and geometry required for EDS with side-entry detectors.

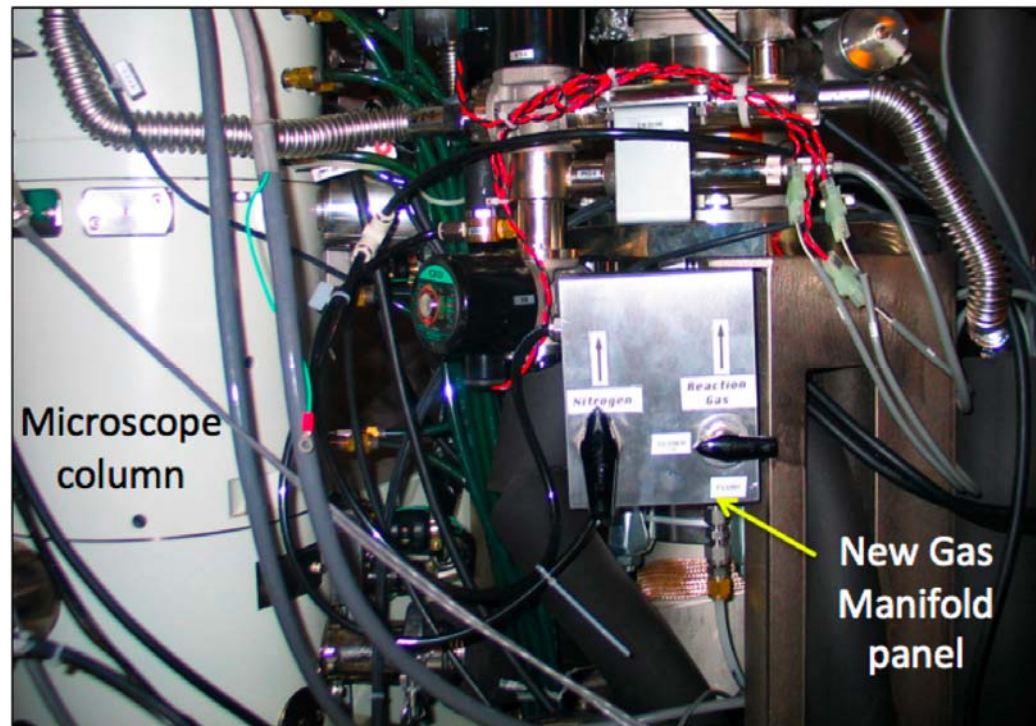
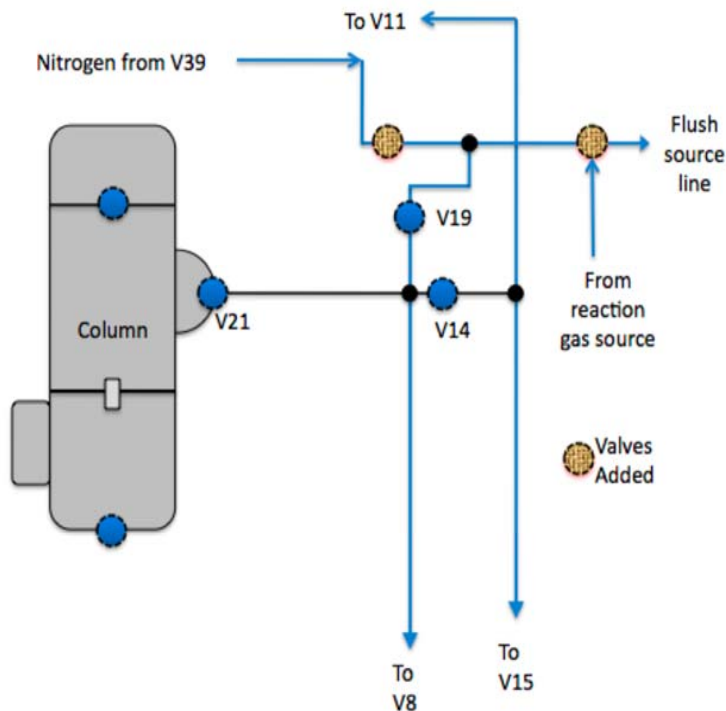


# Development of airlock reaction capability

- Concurrent with our work on E-cell development, we have also developed a new capability for reacting samples in the Protochips heating holder, by using the ACEM airlock as the reactor.
- A gas manifold system was added to the microscope, to permit the choice between standard nitrogen inlet to the airlock, or another gas of choice (e.g. 4% $\text{H}_2$  in Ar) for reaction experiments (e.g. reduction reactions).
- The airlock reaction system replaces to a significant extent our long-time *ex-situ* reactor, because the airlock capability is far more efficient, permitting rapid turn-around for sequential imaging experiments. Its limitation is that gas compositions are limited to non-corrosive mixtures.



# Airlock reaction system



Modified gas inlet system on the JEOL 2200FS ACEM at ORNL, to permit running gas reactions in the specimen airlock with Protochips heating holder.

# Airlock reaction operating scheme

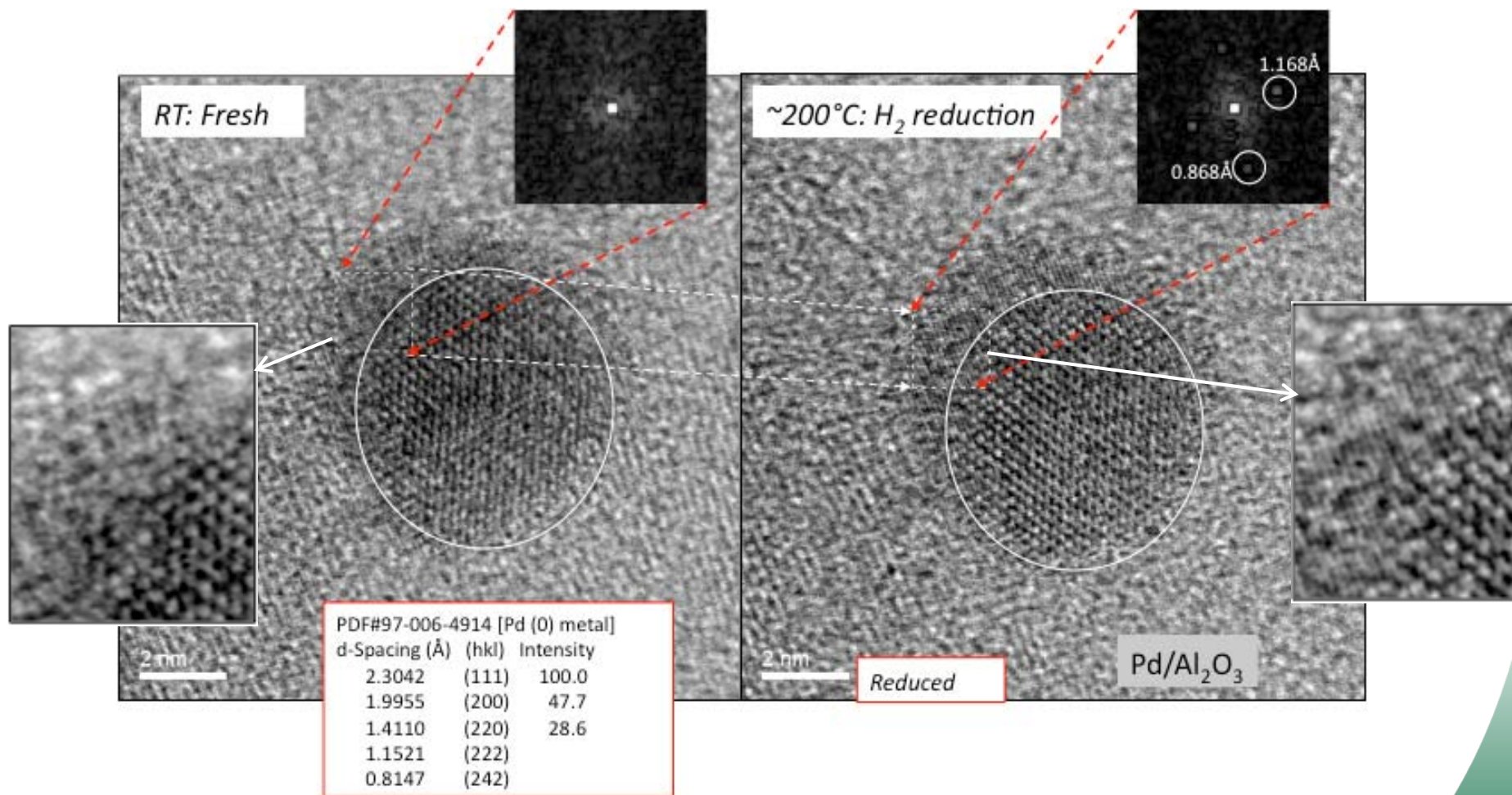
1. Image catalyst at RT. Index areas.
2. Retract Protochips holder into airlock.
3. Admit desired gas into airlock. Cycle several times.
4. Heat catalyst for desired time (instant up, instant down)
5. Standard pump-out, insert holder.
6. Return to indexed locations, make second set of images at RT.
7. Repeat as desired.

## Advantages and disadvantages:

1. + Allows direct imaging using standard heater; not thru upper membrane of E-cell.
2. + Allows easier control of gas to specimen region (i.e. pressure).
3. + Pseudo-ex-situ technique, but much easier than present techniques for ex-situ work, with an order of magnitude faster turn-around
4. – Gas compositions limited to benign compositions (H/Ar, e.g.)

# Reduction reactions in Pd/alumina studies with Eastman Chemical Co.

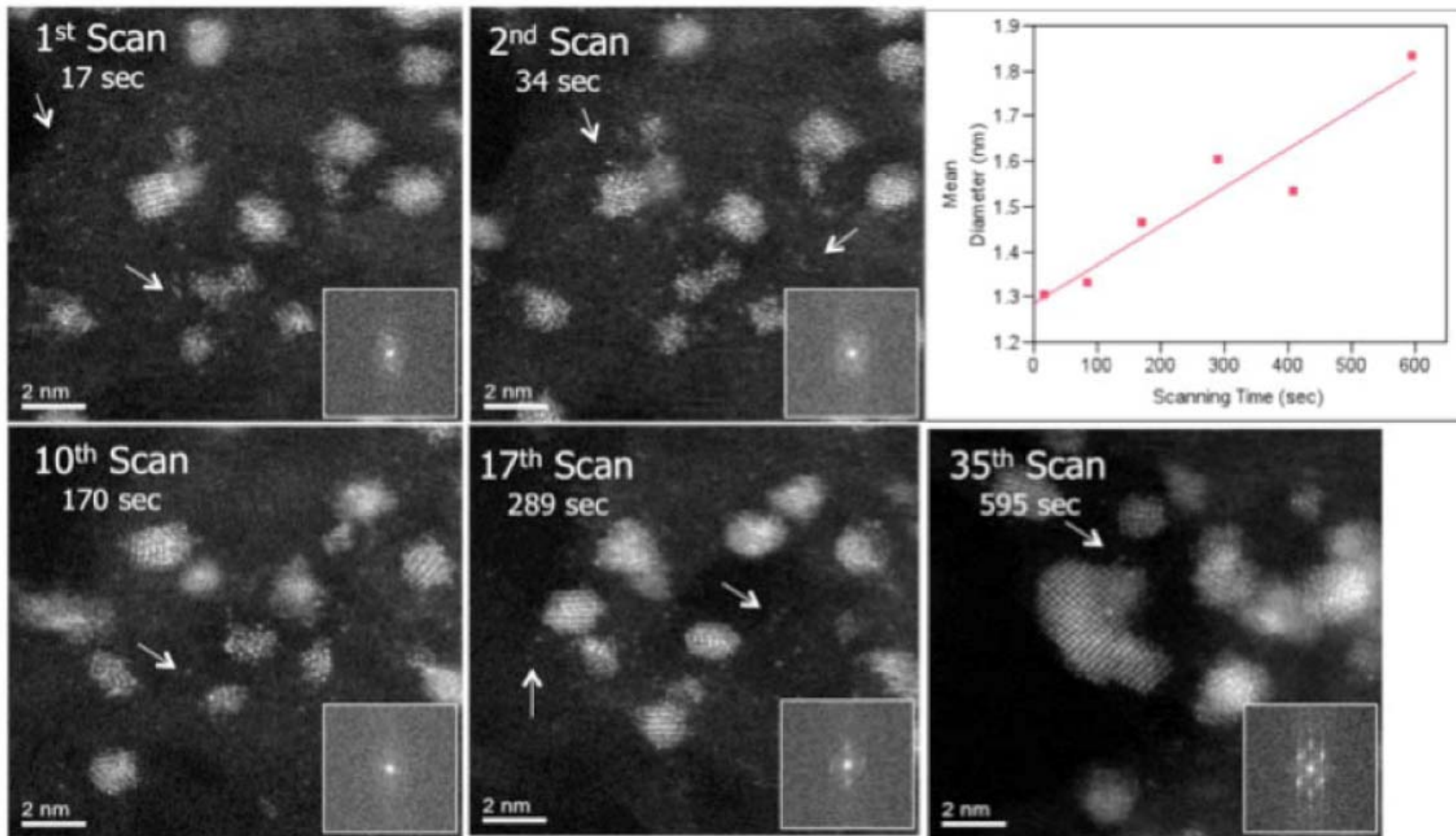
Dr. Louis Germinario, TN Eastman, and Dr. Larry Allard



Pd nanoparticle on alumina support, before (left) and after (right) airlock reduction at  $200^\circ\text{C}$ . Amorphous component at surface shows crystalline lattice after reduction treatment (compare insets). Principal spacing consistent with Pd (222) planes.



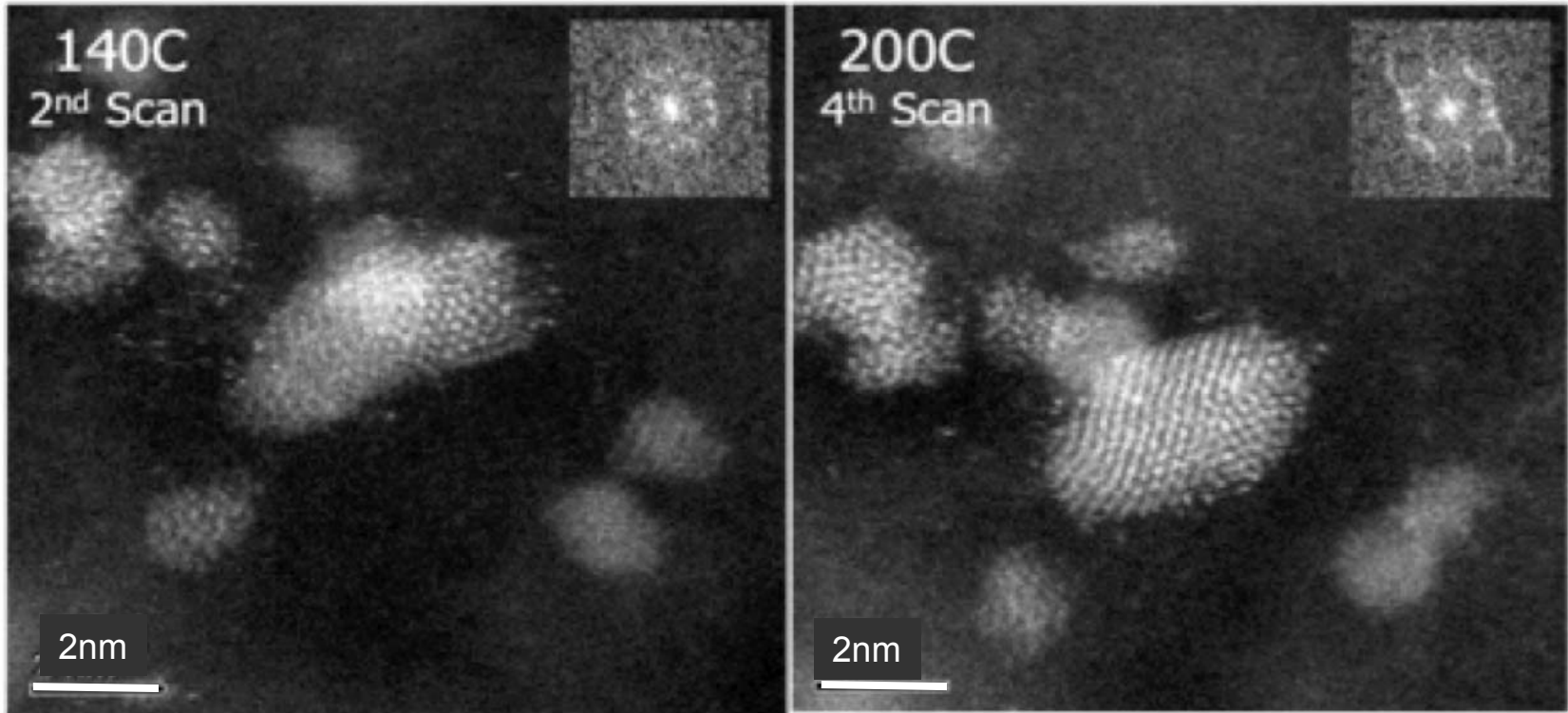
# Eastman Chemicals study of Ru particle sintering: Correlating beam heating with in-situ Protochips heater experiments



Electron irradiation effects on diffusion of single atoms (arrows). Amorphous atom clusters (rafts) grow in size and develop crystalline domains after extensive scanning. Plot show mean particle diameters as highly correlated ( $R^2 = 0.90$ ) with electron scanning times. Sample: ruthenium clusters on carbon support.



# Ru/C behavior at elevated temperature

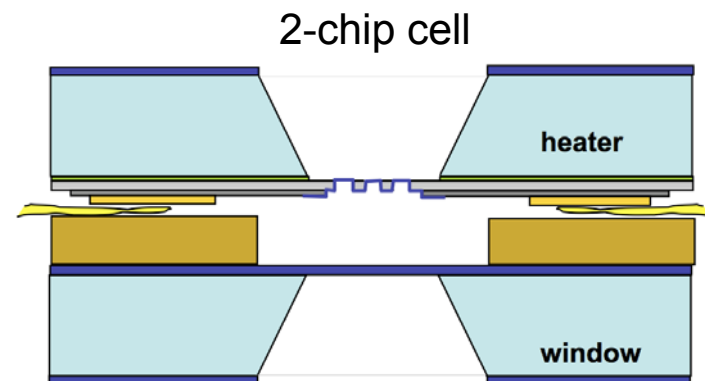
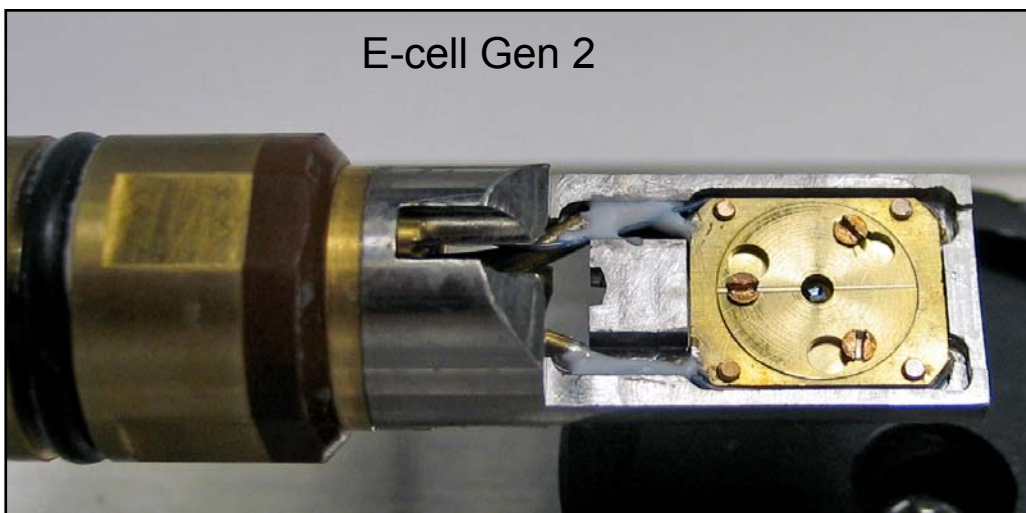
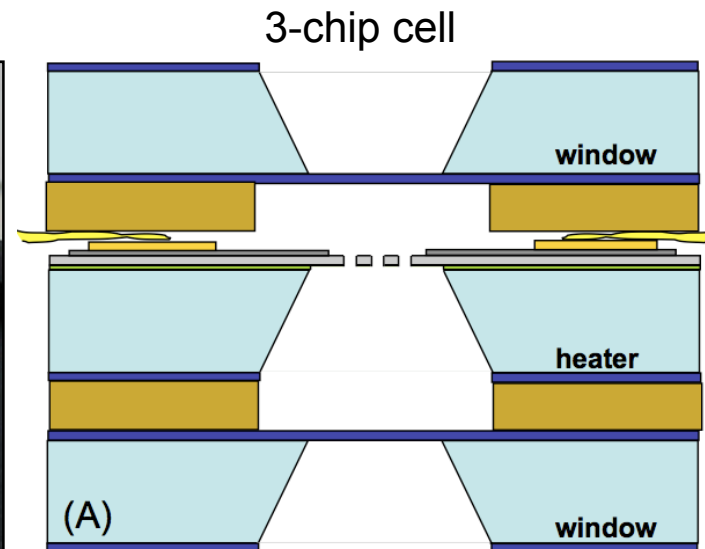
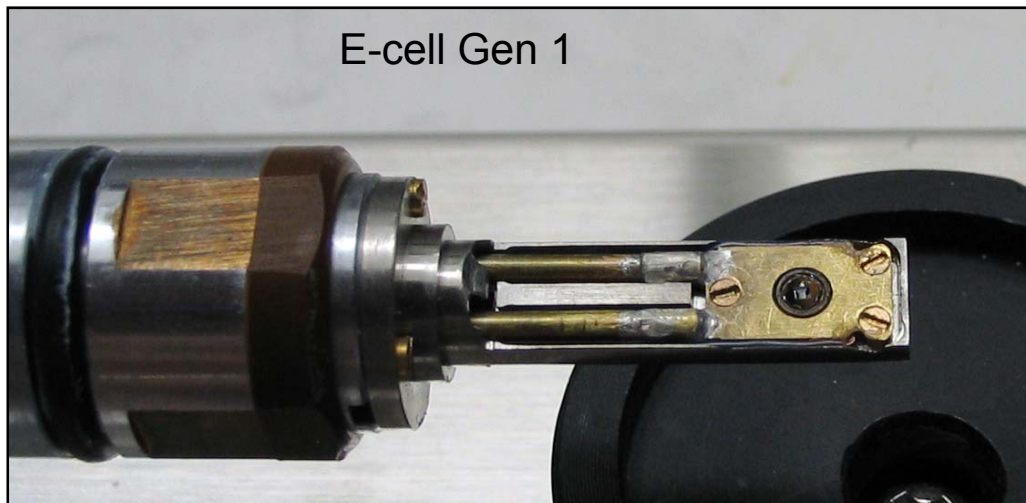


In-situ heating of Ru/C catalyst preparations, in vacuum, provides evidence for a temperature-induced migration, coalescence and ordering at 200°C, that is independent of electron-beam effects.

# Progress in development of an environmental cell (“E-cell”) capability

- The Aduro™ heater chip technology is amenable to use in a special holder designed to allow gases to be passed into a cell with thin windows to sandwich the heater element.
- A “Gen 1” E-cell was fabricated with a 3-chip sandwich, comprising 30nm amorphous silicon nitride windows above and below a standard Aduro™ chip.
- The Gen 1 cell was 1.7mm thick, which proved to be too thick for safe use in the ACEM, which has an objective lens with a 2mm gap.
- A Gen 2 E-cell was then designed that used only 2 chips, with the upper chip being the heater, and the lower chip a thin silicon nitride window.
- With only 2 chips, the Gen 2 E-cell tip is 1.38mm thick, which will allow unimpeded use in the ACEM.
- Preliminary results indicated that the Gen 2 E-cell effectively held atmospheric pressure against vacuum.

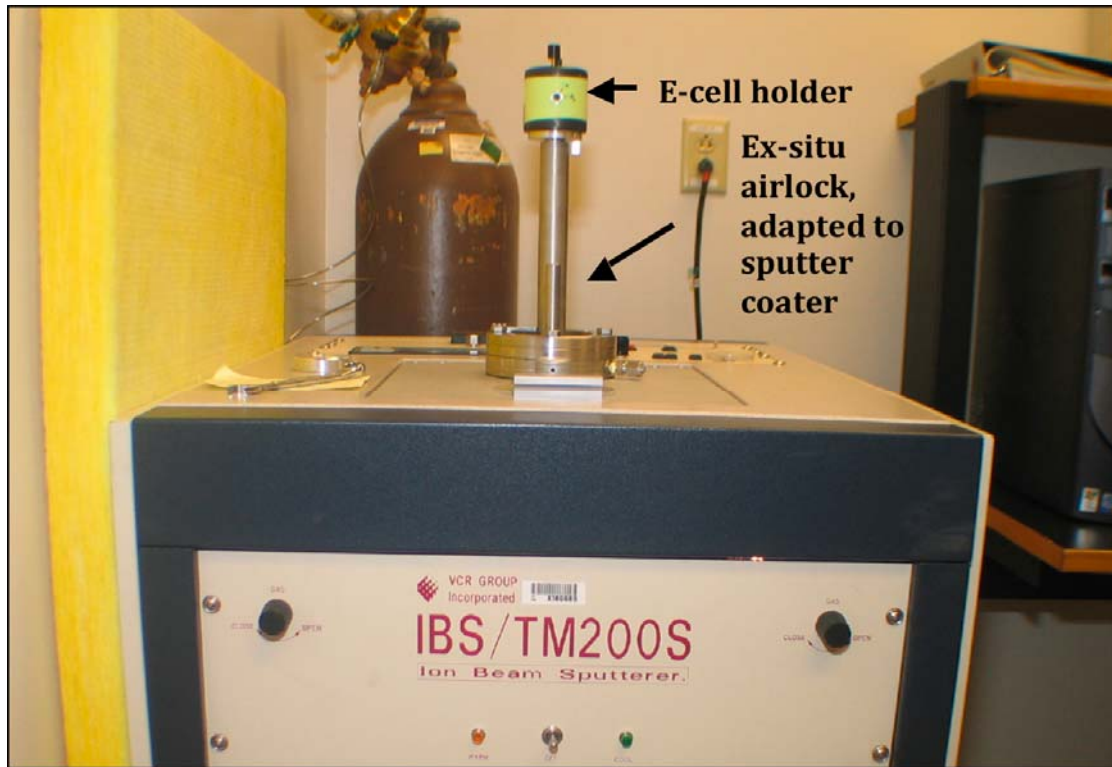
# E-cell development



Gen 1 and Gen 2 E-cell designs. 2-chip stack permits cell 1.38mm thick vs 1.7mm for 3-chip stack. Necessary to fit appropriately in 2mm gap of ACEM objective lens pole piece.

# External E-cell testing station

A means to test the vacuum compatibility of an assembled E-cell prior to insertion into the ACEM was needed. We adapted the airlock entry system from our old ex-situ reactor to the door flange of an existing sputter coating system which is pumped by a turbo pump and achieves vacuums in the low  $10^{-6}$ Torr regime.



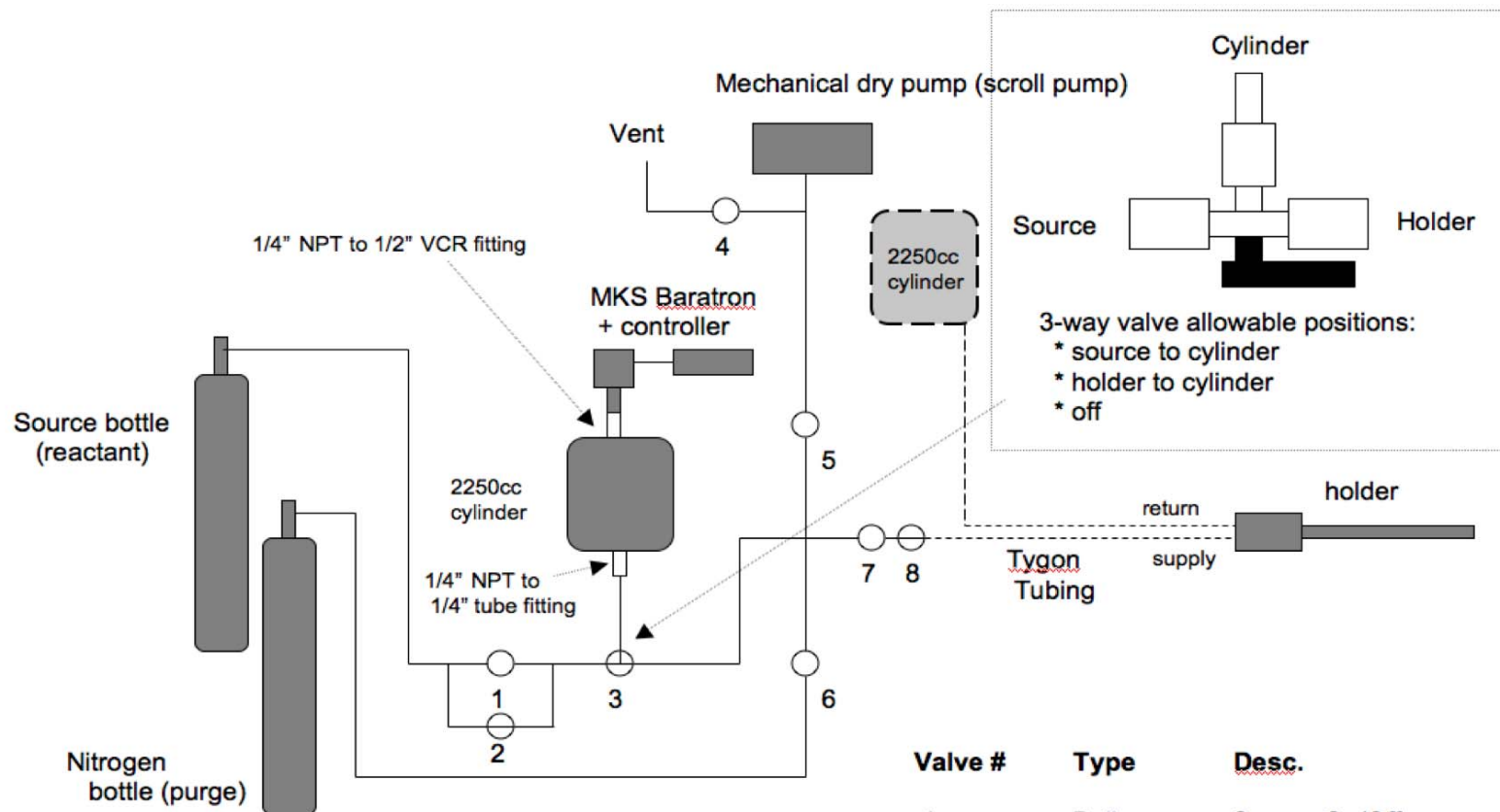
This system allows us to rapidly test the E-cell holder, and to perform experiments to learn how to control our gas handling system.

# A unique gas handling system has been developed permitting accurate pressure control inside E-cell

- Accurate control of gas pressure is critical in reaction experiments, in order to understand kinetics and mechanisms of the behavior of catalytic species.
- The total volume of the E-cell is miniscule, making a direct pressure measurement impossible.
- Our system uses an auxiliary tank to store a chosen gas, and a capacitance manometer gage on the tank to measure the pressure.
- Appropriately sized metering valves allow precise control of the flow of gas into the pressure vessel, and from there into the E-cell.
- Initial reactions will be carried out with a static gas pressure in the range of 20Torr.
- The system will be expanded to add a controlled flow at a measured pressure capability



# Schematic showing layout and operating principle of gas handling system

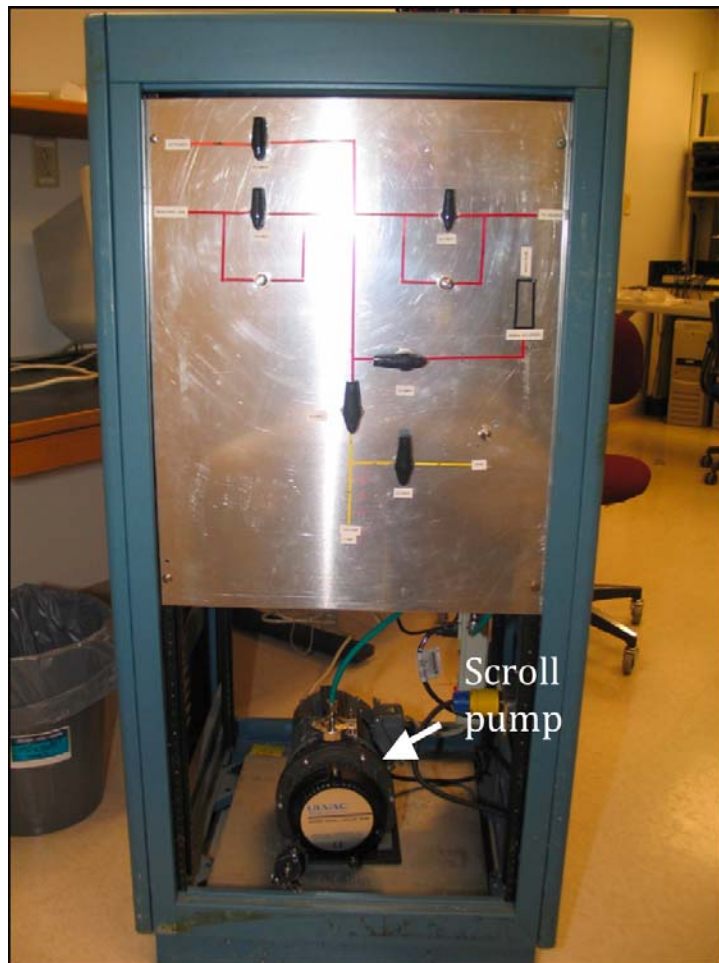


- Ball valve
- ⊖ Needle valve
- ⊕ Three-way valve

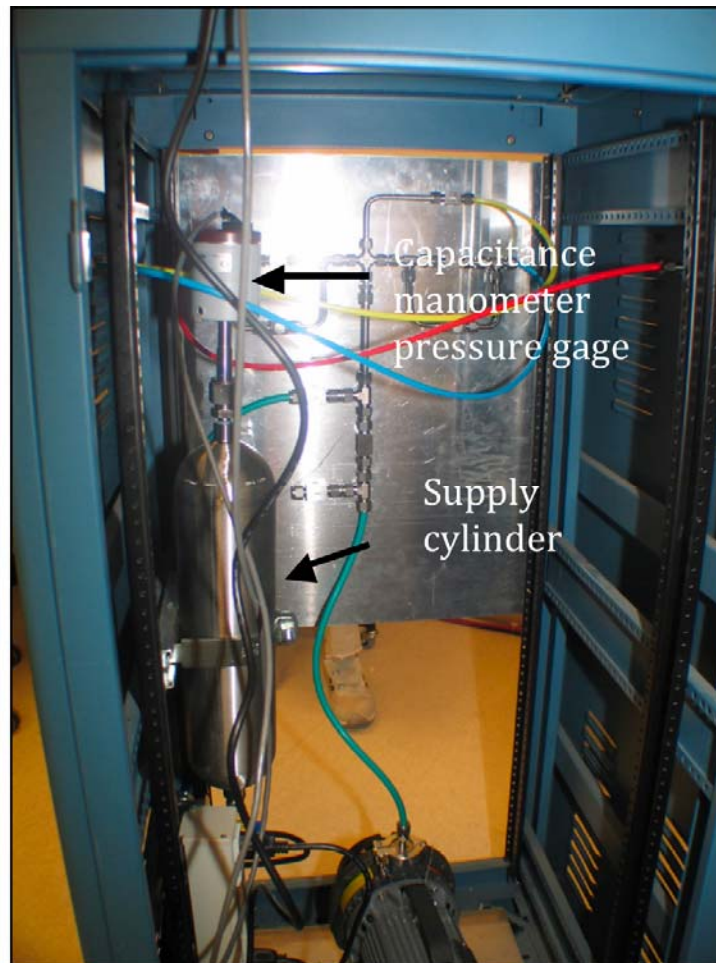
Valve #	Type	Desc.
1	Ball	Source On/Off
2	Needle	Source metering
3	3-way	Bottle / Holder
4	Ball	Vent
5	Ball	Rough
6	Ball	Purge
7	Ball	Holder On/Off
8	Needle	Holder metering

# Views of gas handling system hardware

Front panel showing metering valves



Rear view showing supply cylinder



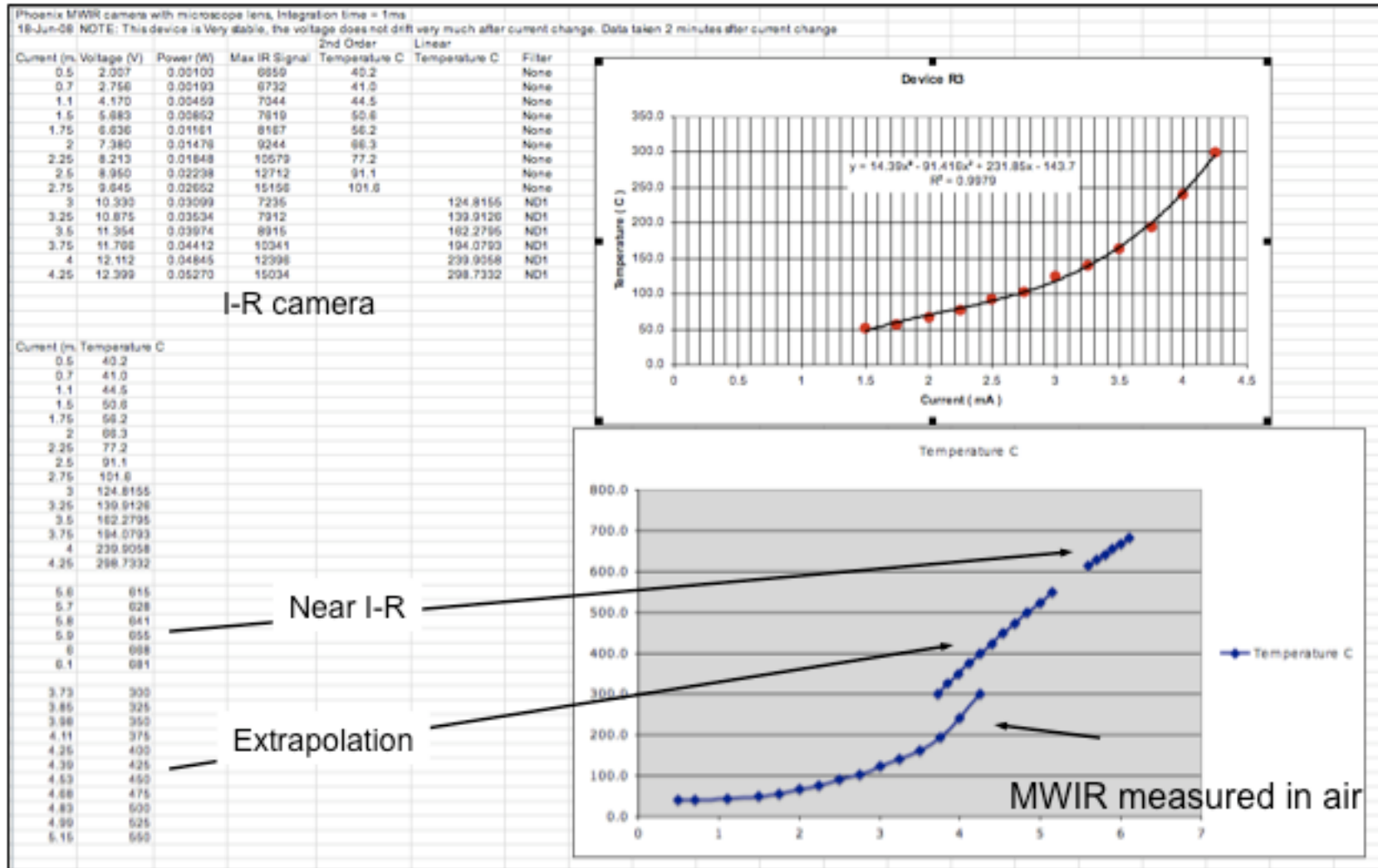
This system has been proved to be extremely easy to operate, and allows control of pressure at the level of  $\pm 1$  Torr.

# Temperature calibration of Aduro™ chips is important for precision reaction experiments

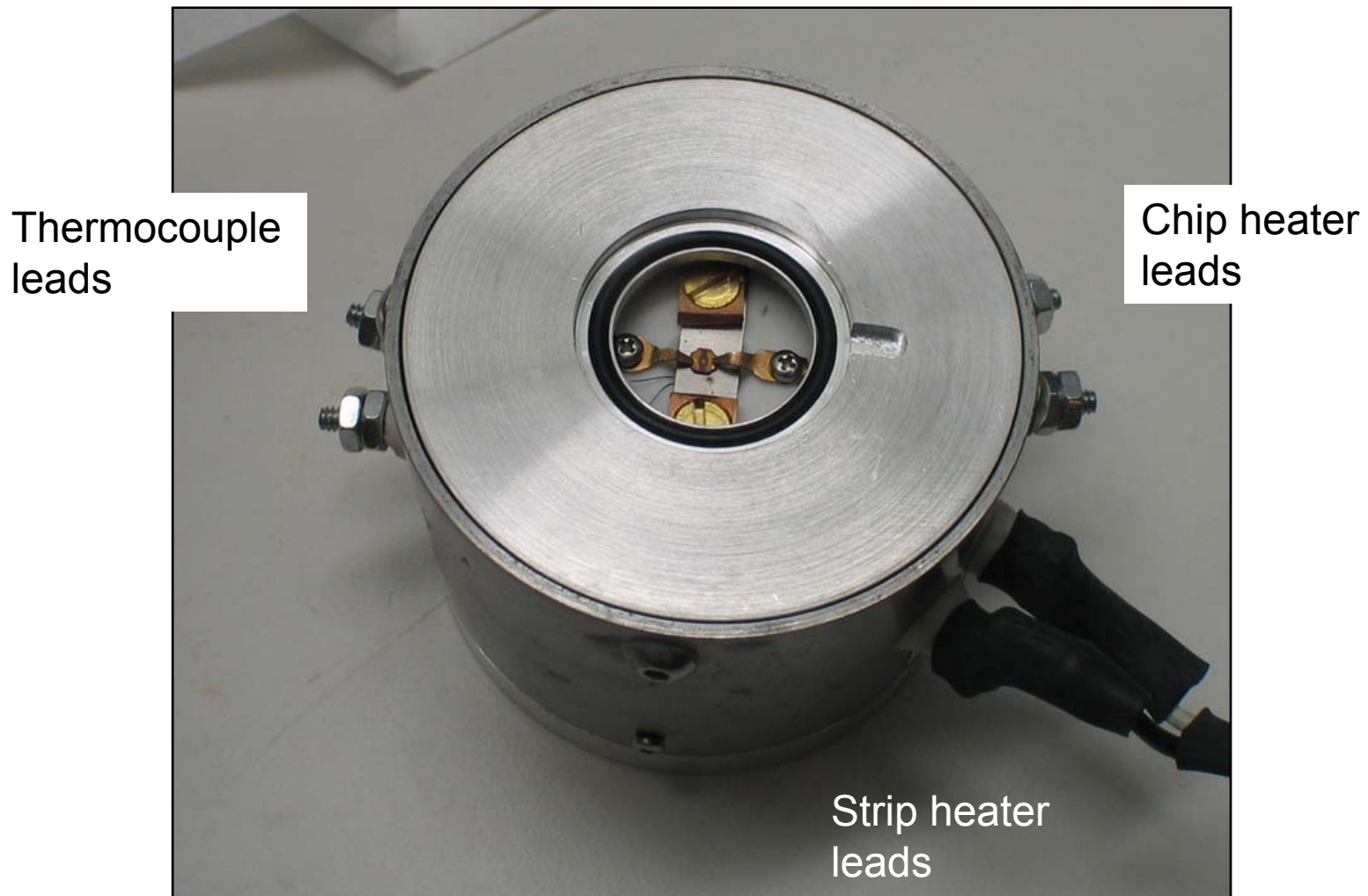
- Protochips provides their Aduro™ devices individually calibrated using a Near Infra-Red optical pyrometer. These calibrations are done from 600° to 1200°C, in vacuum.
- We initially used extrapolations back to 400°C for our early work. However, there is strong demand for conducting reactions at lower temperatures.
- Using HTML's Medium Wavelength I-R camera, we first calibrated trial chips in air, from RT to ~300°C (see next figure).
- It was evident that the low temperature calibrations needed to be done under vacuum.
- We fabricated a chamber to allow appropriate control of the chip temperature while also allowing the MW-IR camera to operate properly.



# Vacuum calibration at high T vs air calibration in lower T range



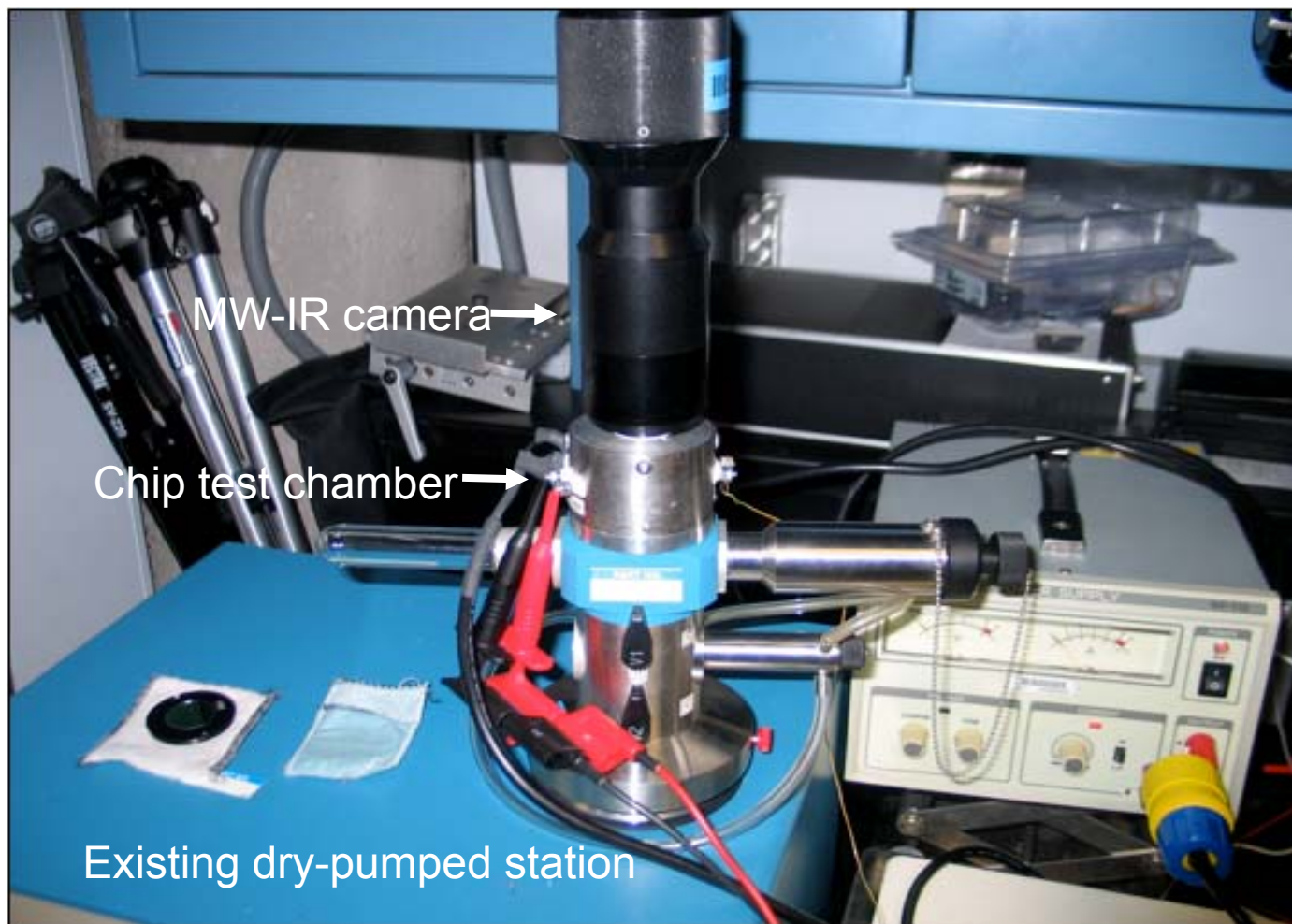
# Vacuum chamber fabricated for low temperature chip calibrations



A strip heater with thermocouple attached is provided to give accurate baseline temperature for the IR camera. The chip can be separately heated.

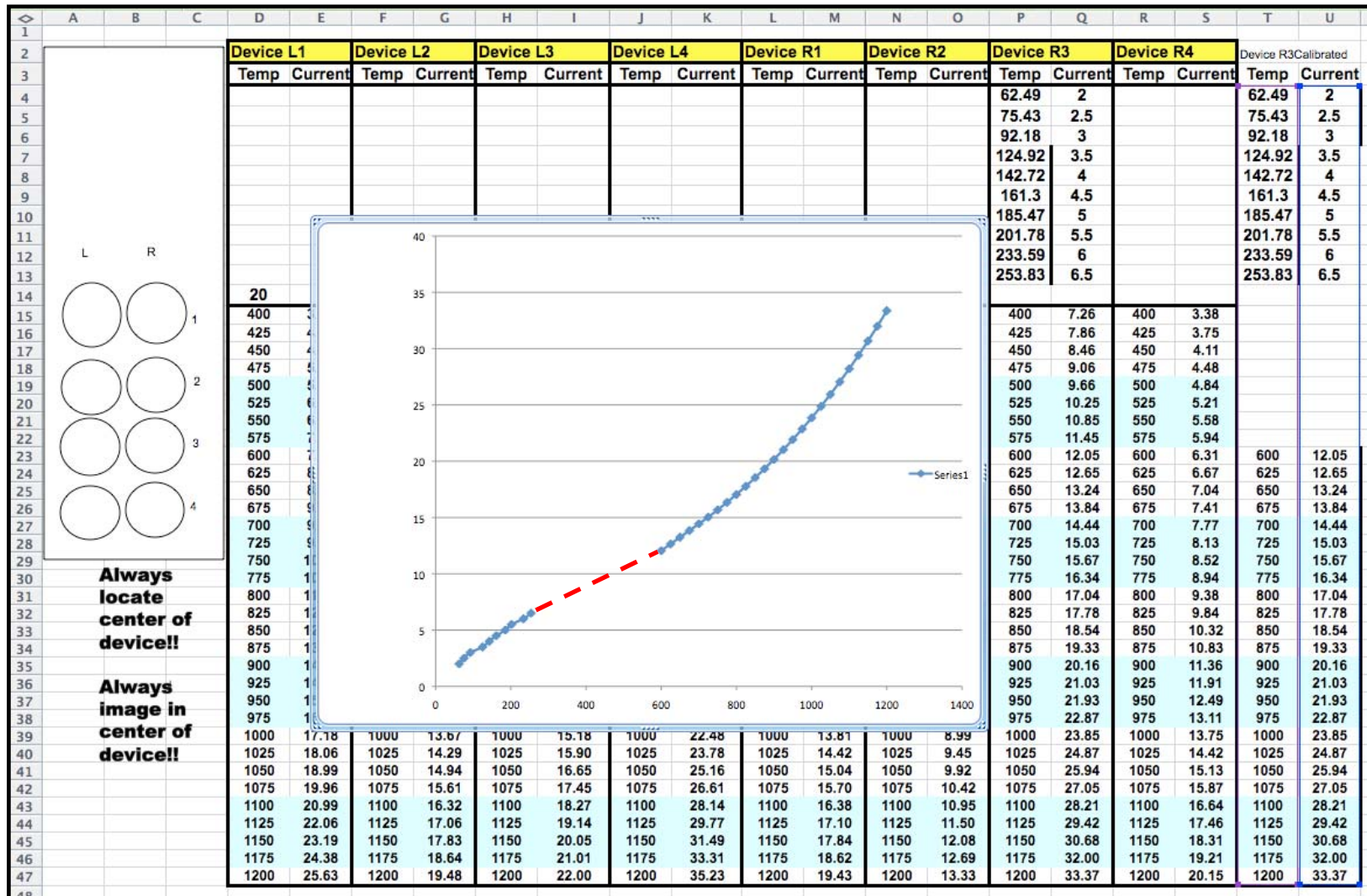
# Temperature calibration experiments

MW-IR camera calibrations will be compared to at least one other technique; Dr. Germinario of Eastman Chemicals will use a scanning thermal probe instrument for direct temperature measurement.





# Example temperature calibration at both high T and low T in vacuum, showing better curve matching



# Other critical considerations for E-cell operation in the electron microscope

- A major question in the conduct of in-situ experiments is “what is the effect of the electron beam on the behavior of the sample, irrespective of any heating experiment?” An example of beam heating effects causing nanoparticle sintering, and the analysis of the sintering phenomena is shown in the following slides.
- We have initiated a project with Prof. Abhaya Datye of UNM to study the phenomenon of nanoparticle melting as a measure of actual temperature under a combination of beam heating and Protochips Aduro™ heating. Nanoparticles exhibit lowered melting temperatures dependent upon particle size.
- Correlating high-resolution SEM measurements of nanoparticles on heated bulk substrates with ACEM images of corresponding size nanoparticles may provide an accurate indication of absolute temperatures under the electron beam.

# Pt nanoparticle sintering phenomena



Our images were featured on this  
MRS Bulletin cover in February 2008

## Coalescence and Sintering of Pt Nanoparticles: In-situ Observation by Aberration-Corrected HA-ADF STEM

M.A. Asoro<sup>1</sup>, D. Kovar<sup>1,2</sup>, Y. Shao-Horn<sup>3,4</sup>, L.F. Allard<sup>5</sup>, P.J.  
Ferreira<sup>1,2\*</sup>

<sup>1</sup>Materials Science and Engineering Program

<sup>2</sup>Department of Mechanical Engineering  
University of Texas at Austin, Austin, TX, 78712, USA

<sup>3</sup>Department of Mechanical Engineering

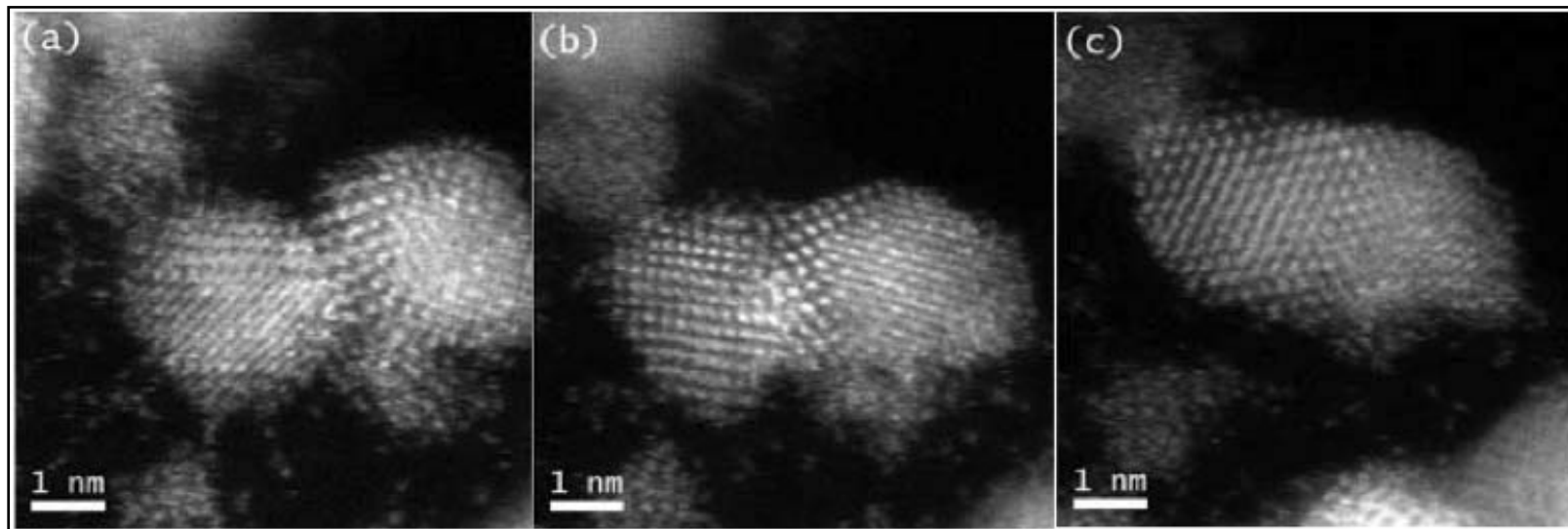
<sup>4</sup>Department of Materials Science and Engineering  
Massachusetts Institute of Technology Cambridge, MA, 02139,  
USA

<sup>5</sup>Materials Science and Technology Division,  
Oak Ridge National Laboratory Oak Ridge, TN, 37831, USA

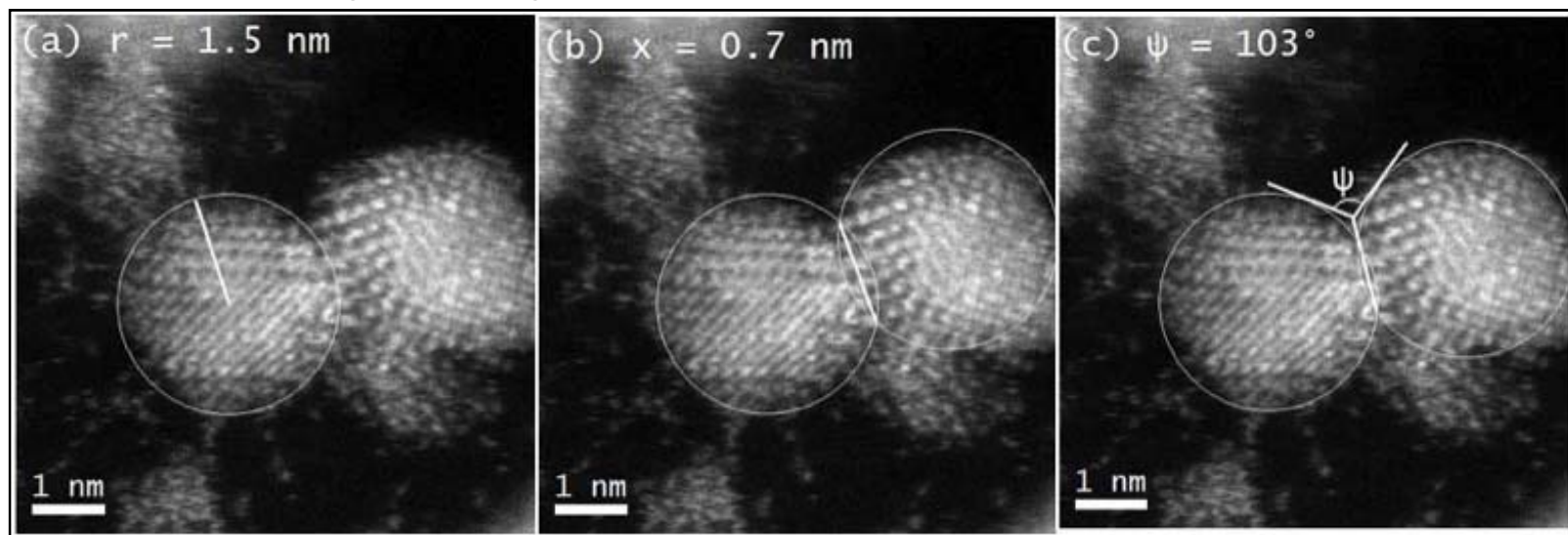
Full article submitted to "Nanoletters"  
March 9, 2009



# Analysis of nanoparticle sintering under beam heating

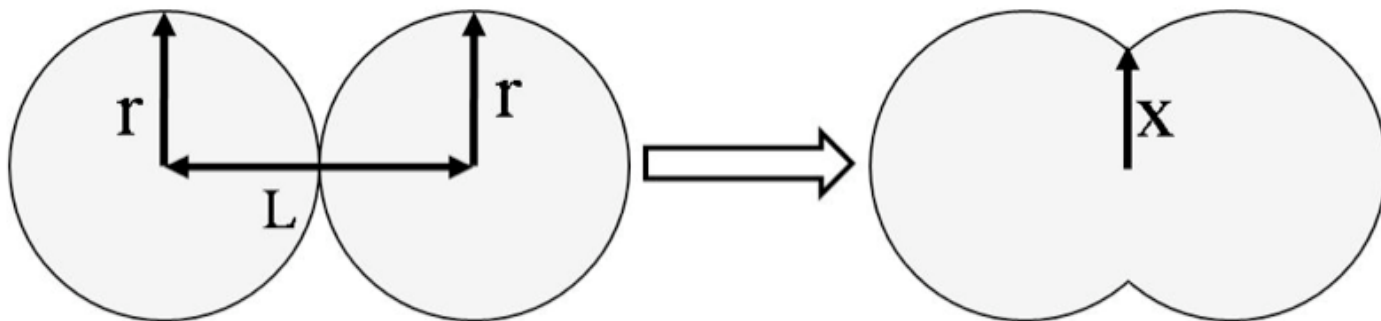


Pt nanoparticles sintering under electron beam heating effects. Total electron dose carefully monitored over image recording sequence.

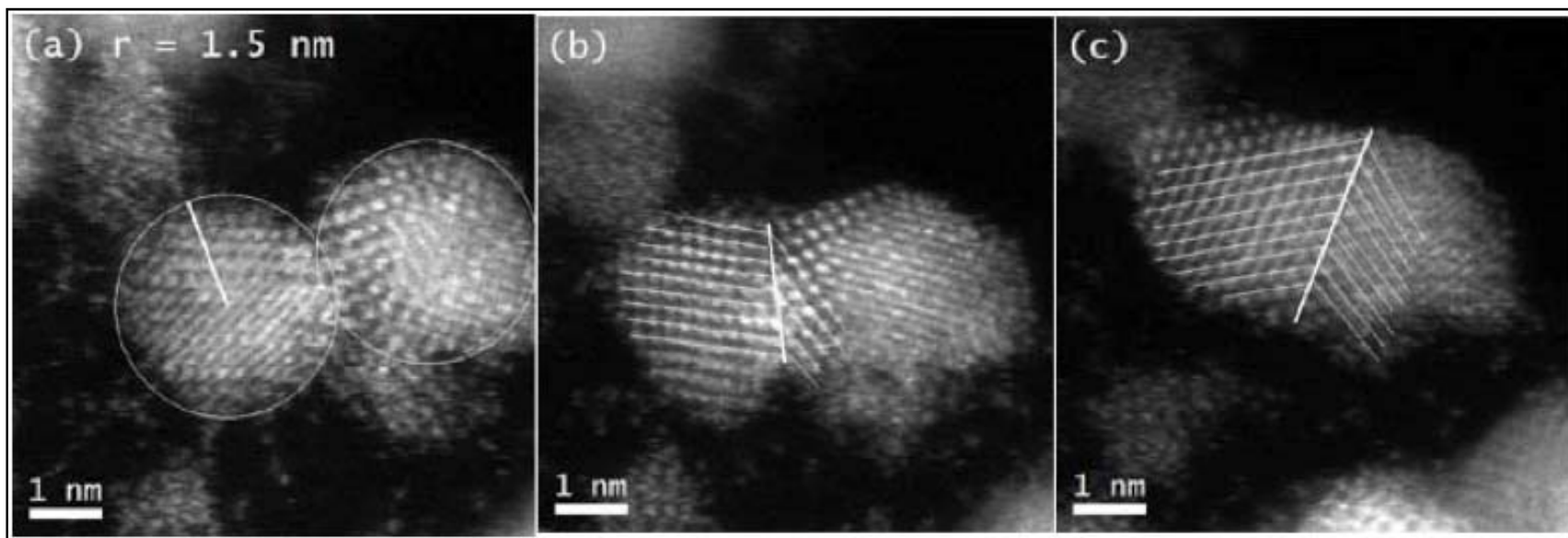


From image (a), illustration of the measurements of (a) particle radius (b) neck radius (c) dihedral angle

# Direct measurements of sintering parameters



Schematic of sintering of a pair of spherical particles



Particle radius

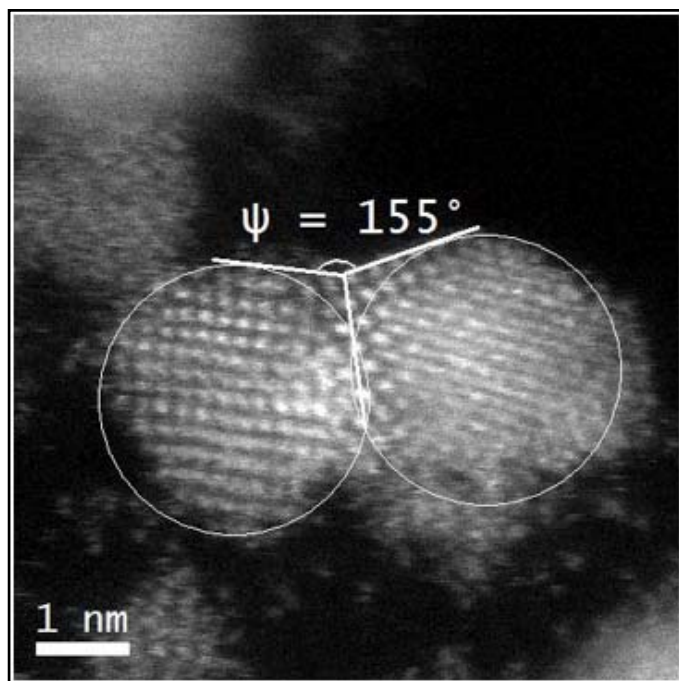
Grain boundary diam 1

Grain boundary diam 2



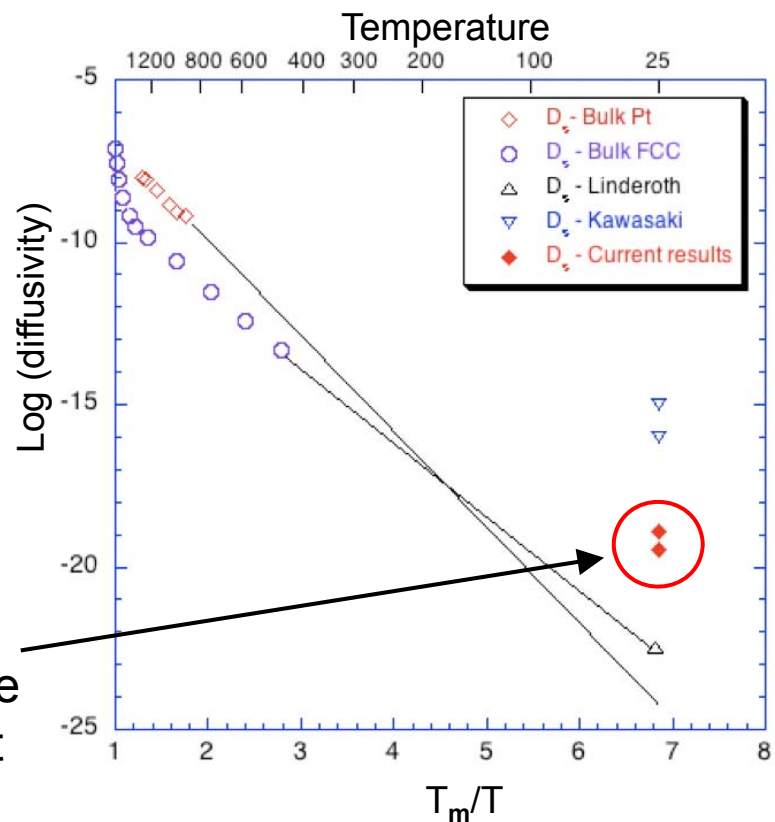
# Particle measurements

Values from preceding images



Dihedral angle  $\psi$

<b>Sintering Time, <math>t</math> (sec)</b>	15	50
<b>Particle radius, <math>r</math> (nm)</b>	1.5	1.5
<b>Neck radius, <math>x</math> (nm)</b>	0.7	0.9
<b><math>x/r</math></b>	0.467	0.643
<b><math>\Psi</math> (°)</b>	103	155



Our values for surface diffusivities are in reasonable agreement with other experimental methods, showing the value of HREM in correlating measurements at the nanoscale with bulk phenomena.

# Plans for FY2009-FY2010

- Continue work started FY 2008 in development of in-situ heating and gas reaction capabilities for catalyst reaction studies via aberration-corrected electron microscopy.

- leverage funding with Protochips Co. via phase II SBIR support (with possibility for additional funding in FY2009 thru BES).

- Utilize new in-situ capabilities for studies of the behavior of highly dispersed catalytic species on a variety of support materials, and nanoparticulates of controlled composition, to understand the changes in catalyst morphology as a function of treatment conditions, and ultimately the factors that control degradation of catalyst performance with use.

- Continue collaborations underway with top-line industry and university researchers

- Initiate new work with industry collaborators (UOP, Eastman Chemicals), leveraging funding via WFO projects.

# Milestones

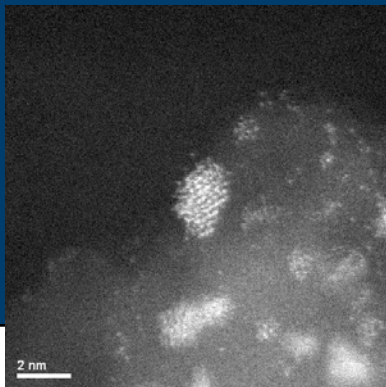
- Mar-09: Fabricate a glovebox facility with CCTV camera and airlock pass-thru to permit loading and transfer of air-sensitive catalysts to ACEM
- June-09: Test a new silicon drift x-ray detector system on consignment from Bruker Co. for use on the ACEM, to characterize catalyst compositions at elevated temperatures.
- Oct-09: Design and fabricate a prototype 'double-tilt' heating holder for the ACEM, required to permit accurate orientation of crystalline supports for more reliable characterizations.
- Dec-09: Utilize our Protochips heater for the Hitachi TEM to conduct trial studies of bimetallic catalysts using EDS analysis and electron holography.
- Mar-10: Develop protocols for most effective use of E-cell in imaging experiments to study gaseous reaction phenomena.
- Sept-10: Submit for publication at least 6 articles in refereed journals on catalyst research activities.

# Principal Technical Accomplishments

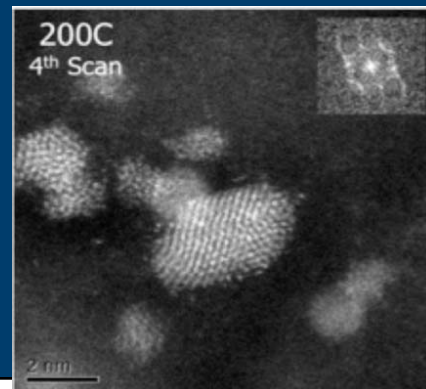
- Prototype Gen 1 E-cell fabricated and tested, providing guidance for design of Gen 2 E-cell.
- Prototype Gen 2 E-cell fabricated.
- Airlock reaction system conceived, fabricated and tested successfully.
- Ex-situ vacuum test stand system developed and tested successfully.
- Gas control system designed, fabricated and tested successfully.
- Prototype heater holder for Hitachi TEM designed, fabricated and tested successfully.
- Numerous protocols for the conduct of heating experiments in the ACEM were conceived and tested, leading to a sound foundation for future catalyst reaction studies.
- Our work has resulted in numerous invited and contributed publications and presentations.

Summary: our work supports many entities...

PNNL



Eastman Chemicals,...



Industry...

University...



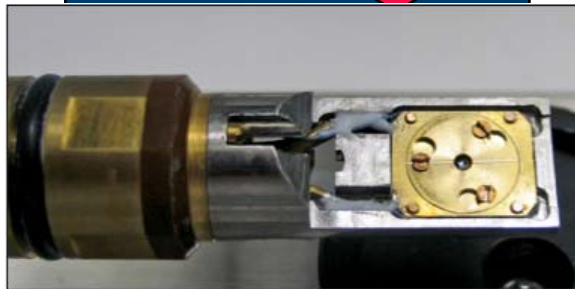
UT-Austin,...



ACEM



ORNL



Protochips